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(54) **MICROCELLULAR FOAM**
MIKROZELLSCHAUM
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(56) References cited:

EP-A- 0 098 712	EP-A- 0 585 147
DE-A- 4 201 763	GB-A- 1 210 626
US-A- 3 766 099	US-A- 4 217 319
US-A- 4 640 933	US-A- 4 694 027
US-A- 4 699 134	

- **DATABASE WPI Section Ch, Week 9105 Derwent Publications Ltd., London, GB; Class A17, AN 91-033663 XP002077037 & JP 02 303815 A (JSP CORP) , 17 December 1990**
- **DATABASE WPI Section Ch, Week 9211 Derwent Publications Ltd., London, GB; Class A17, AN 92-083702 XP002077038 & JP 04 025533 A (SEKISUI PLASTICS CO LTD) , 29 January 1992**

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The file contains technical information submitted after the application was filed and not included in this specification

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Description

[0001] The present invention relates to a process for preparing a non-crosslinked polyolefin foam elongated cellular body having a fine-celled closed structure, and to a non-crosslinked fine-celled foam product.

[0002] Non-crosslinked foams in the prior art made with the herein described extrusion accumulator process typically had cells within the 7.9 to 11.8 cells/cm (20 to 30 cells per inch) range. Attempts to make the non-crosslinked thick cross-sectional foams with a higher cell count resulted in non-flat/wavy foam, voids, ripples, or the like.

[0003] U.S. Patent No. 4,694,027 discloses a process for preparing a substantially closed cell olefin polymer foam having dimensional stability comprising the steps of (a) heat plastifying an olefin polymer resin selected from the group consisting of homopolymers of ethylene and copolymers of ethylene and a copolymerizable monomer, (b) admixing said heat plastified resin with (1) a fatty acid compound stability control agent and (2) a blowing agent including isobutane, and (c) activating said blowing agent to expand said admixture to a substantially closed-cell olefin polymer foam. Example 2 of this patent discloses a foam having a cell count of approximately 1.26 cells/cm (3.2 cells per inch).

[0004] The main object of the invention is to solve the problems of the above stated prior art and to provide a non-crosslinked foam product, which offers the properties of a crosslinked foam product, but with a finer cell count greater than 19.7 cells/cm (50 cells per inch) and a soft, non-abrasive feel while providing capability to be recycled, which is extrinsic to a crosslinked foam product. Other objects and advantages of the invention are set out herein or are obvious herefrom to one skilled in the art.

[0005] The present invention provides a process for preparing a non-crosslinked polyolefin foam elongated cellular body having a fine-celled dosed structure, said fine-celled structure having a cell count greater than 19.7 cells/cm (50 cells/inch), said process comprising the steps of melting a polyolefin; forming a mixture of said polyolefin, and an amount of a fatty acid compound permeability control agent; dissolving an effective amount of a blowing agent in said mixture to form a blowing agent-containing mixture; transferring said blowing agent-containing mixture into a zone of lower pressure and temperature; and permitting said blowing agent-containing mixture to expand in the zone of lower pressure and temperature to produce said elongated cellular body, said process being characterized by the steps of:

melting a copolymer of an olefin monomer and an ethylenic monomer different from the monomer of said polyolefin with said polyolefin to form a polymeric blend before the step of forming said mixture, the amount of said copolymer being in the range of from 5 to 25 percent by weight of said blend;

adding an amount of a nucleating agent sufficient to produce a cell count greater than 19.7 cells/cm (50 cells/inch) to said mixture before the step of dissolving said blowing agent; and

after said step of dissolving, extruding said blowing agent-containing mixture into a holding zone; and maintaining said holding zone at conditions, including temperature and pressure, at which said blowing agent-containing mixture does not foam.

[0006] The present invention further provides a non-crosslinked fine-celled foam product comprising:

a polymeric structure being substantially composed of fine cells and having the cell count being greater than 19.7 cells/cm (50 cells/inch), said polymeric structure being a blend of a polyolefin and a copolymer of an olefin monomer and an ethylenic monomer different from the monomer of said polyolefin, the amount of said copolymer being in the range of from 5 to 25 percent by weight of said blend.

[0007] Preferred embodiments of the present invention are set forth in the sub-claims.

[0008] According to the invention a blended non-crosslinked polyolefin composition is used which is processable into a foamed product, preferably a foamed plank, comprising a polyolefin, a copolymer of an olefin and a different ethylenic monomer, an effective amount of a fatty acid compound permeability control agent, and an effective amount of a nucleating agent. The non-crosslinked foamed product of the invention offers the properties of a crosslinked foam product and has a finer cell count greater than 19.7 cells/cm (50 cells per inch) and a soft, nonabrasive feel. The non-crosslinked foamed product has the capability of being recycled, which is extrinsic to a crosslinked foamed product. To improve the softness of the foam product, the copolymer is preferably a copolymer of an olefin and an ester monomer. To improve the strength and/or stiffness of the foam product, an ionomer resin can be included in the blend. Isobutane blowing agent is also usually present in an amount of from 5 to 30 parts, best from 10 to 20 parts, per 100 parts of the polymer blend composition during the operation/process of preparing the foam.

[0009] Preferably the polyolefin is polyethylene. Preferably the copolymer is ethylene vinyl acetate copolymer or ethylene methyl acrylate copolymer. Preferably the fatty acid compound permeability control agent is glycerol monostearate. Preferably the nucleating agent is (a) crystalline silica, or (b) sodium bicarbonate-citric acid, or (c) talc.

[0010] In the most preferred blended polymer composition the polyolefin is low density polyethylene, the copolymer is ethylene methyl acrylate copolymer, the fatty add compound permeability control agent is glycerol monostearate

and the nucleating agent is crystalline silica.

[0011] The invention also involves a process for preparing an expanded non-crosslinked low or high density polyolefin foam, which offers the properties of a crosslinked foam product, with a finer cell count greater than 19.7 cells/cm (50 cells per inch) and a soft, non-abrasive feel while also providing capability to be recycled, whereas crosslinked foam does not. The process includes forming a mixture of a polyolefin and a copolymer of an olefin and a different ethylenic monomer, an effective amount of a fatty acid compound permeability control agent, an effective amount of a nucleating agent and an effective amount of isobutane blowing agent, dissolved in the polyolefin and copolymer, under pressure. The mixture has a temperature at which the viscosity of the mixture is sufficient to retain the blowing agent when the mixture is allowed to expand. The mixture is extruded into a holding zone maintained at a temperature and pressure which does not allow the resulting mixture to foam. The extrusion is done without an extrusion die. The holding zone has an outlet die defining an orifice opening into a zone of lower pressure at which the mixture foams. An openable gate closes the die orifice and periodically the gate is opened and substantially concurrently therewith mechanical pressure is applied by a movable ram of the mixture to eject the mixture from the holding zone through the die orifice into the zone of lower pressure, at a rate greater than that at which substantial foaming in the die orifice occurs and less than that at which substantial irregularities in cross-sectional area or shape occurs. The ejected mixture is permitted to expand unrestrained in at least one dimension to produce an elongated cellular body.

[0012] In the invention process, using the accumulator process described in U.S. Patent No. 4,323,528, flat fine-celled closed plank structures can be produced.

[0013] The invention further involves an expanded non-crosslinked low or high density polyolefin foam having a fine-celled dosed structure, which is prepared by the invention process.

[0014] The invention foam is a plank foam with dimensions of typically 274.3 cm by 61.0 cm by 5.1 cm (or 7.6 cm) (108 inches by 24 inches by 2 inches (or 3 inches)). The invention foam will replace bun stock crosslinked foam. Manufacturers of such crosslinked foam include Sentinel, Voltek, and Monarch Rubber Company. The invention foam is a fine-cell (microcellular), soft material. The invention foam is preferably made with low density polyethylene, ethylene vinyl acetate or ethylene methyl acrylate, isobutane blowing agent, a fatty acid (glycerol monostearate) to prevent collapse of the foam, and a nucleating agent, for example, crystalline silica or sodium bicarbonate-citric acid or talc. The invention non-crosslinked foam compares favorably to many of the physical characteristics of a crosslinked foam. However, unlike crosslinked foam, the invention foam is recyclable.

[0015] The invention involves non-crosslinked polyolefin foam which offers the properties of a crosslinked product with fine-celled (microcellular) structure with cell counts greater than 19.7 cells/cm (50 cells per inch) and a soft, non-abrasive feel while also providing capability to be recycled (whereas crosslinked foam does not).

[0016] The foamed product is prepared from a blend of a polyolefin and a copolymer of an olefin and a different (nonionic) ethylenic monomer. Preferably the polyolefin is a low density ethylene homopolymer. Preferably the copolymer is an ethylene vinyl acetate copolymer or an ethylene methyl acrylate copolymer. The copolymers are usually soft or have low stiffness.

[0017] Examples of the thermoplastic polyolefins are polyethylenes and polypropylenes. The polyethylenes can be HOPE, MDPE, LDPE and LLDPE.

[0018] Examples of the ethylene copolymers are ethylene vinyl acetate copolymers, ethylene-1-butene copolymers, ethylene methyl acrylate copolymers, and ethylene-acrylic acid copolymers.

[0019] The amount of the polyolefin in the polymer blend typically is 5 to 95 percent, preferably about 85 percent based on the total weight of the polymer blend composition (excluding the blowing agent).

[0020] The amount of the copolymer of an olefin and a different ethylenic monomer in the polymer blend is 5 to 25 percent, preferably about 12 percent, based on the total weight of the polymer blend composition (excluding the blowing agent). In the copolymer, the different ethylenic monomer is preferably used in the amount of 5 to 20 percent, based on the total weight of the copolymer.

[0021] To improve softness, copolymers containing esters, such as, ethylene methyl acrylate (EMA) or ethylene vinyl acetate (EVA), can be added to the mixture with a total ester monomer content of the final product (or the polymer blended composition, excluding the blowing agent) in the range of up to 20 percent, preferably about 2.4 percent, to allow best control of the process.

[0022] The melt indices for some of the preferred components used in the invention blends are:

Material	Melt Index (g/10 min.)
EMA	2.0
EVA (UE 630)	1.8
PE	1.8 - 2.2

[0023] A fatty acid compound permeability control agent is added to the polymer blend composition to enhance

dimensional stability in the foam product Preferred fatty acid compound permeability control agents include amides and esters of C₁₂₋₂₄ fatty acids. Such permeability control agents are taught in U.S. Patent Nos. 3,644,230 and 4,214,054. Preferred individual permeability control agents include steryl stearamide, glycerol monostearate, glycerol monobenhenate, and sorbitol monostearate. The most preferred permeability control agent is glycerol monostearate. Typically, such fatty acid compound permeability control agents are employed in an amount ranging from 0.1 to 5 parts per hundred parts of the polymer blend composition (excluding the blowing agent), or preferably about 1.5 weight percent based on the polymer blend composition (excluding the blowing agent) to prevent foam collapse.

[0024] The fatty acid compound permeability control agents include partial esters of long chain fatty acids with polyols, fatty acid amides, and complete esters of fatty acids. Some further examples thereof are glycerol distearate, glyceryl monobenzoate and sorbitan monooleate.

[0025] The nucleating agent is used to regulate cell size within the foam. The nucleating agent preferably is (a) crystalline silica, or (b) sodium bicarbonate citric acid, or (c) talc. The most preferred nucleating agent is crystalline silica and is typically used in amounts of 10 to 25 percent by weight, most preferably 13 to 17 weight percent, based upon the weight of the total composition (excluding the blowing agent). The preferred sodium bicarbonate-citric acid nucleating agents are commercially available under the trademark HYDROCEROL. The preferred sodium bicarbonate-citric acid is Hydrocerol CF-70 or Hydrocerol CF-40 (a particulate/powder of, respectively, a 70 or 40 percent concentration of sodium bicarbonate and citric acid in a wax and polyethylene base in pellet form). The nucleating agent is typically used in amounts of from 0.1 to 5 percent by weight, preferably 0.2 to 2 percent by weight, most preferably about 0.5 weight percent, based upon the weight of the total composition (excluding the blowing agent).

[0026] In U.S. Patent No. 4,572,740 (column 3, line 18), it is disclosed that "hydrocerol" nucleating agent is also a blowing agent. The melt temperature (i.e., approximately, 105°C (220°F)) of the invention is well below the temperature in U.S. Patent No. 4,572,740. Therefore, the "hydrocerol" nucleating agent is purely a nucleating agent in the invention process.

[0027] Other nucleating agents, such as, clay, mica, titanium oxide, zinc oxide, calcium silicate, and metallic salts of fatty acids such as barium stearate, zinc stearate and aluminum stearate, can be used. Nucleating agents are usually finely divided and may be pelletized, or encapsulated.

[0028] The polymer blend composition can also contain up to 10 percent, preferably about 3 percent, based upon the total weight of the polymer blend composition (excluding the blowing agent), of an ionomeric resin. The ionomeric resin is a cation initiated crosslinked polymer of ethylene and a vinyl acid, preferably a zinc or sodium ion initiated crosslinked polymer of ethylene and methacrylic acid. An ionomer is a thermoplastic polymer that is ionically crosslinked to form bonds between the acid groups within a chain and neighboring chains. The ionomers improve the strength and/or the stiffness of the microcellular foam planks. In general, ionomers are transparent, resistant to abrasion and solvents, have excellent electrical properties, and have outstanding puncture and low temperature impact resistance. Ionomeric resins are recyclable. (Note that the ionomeric resin is not a crosslinking agent regarding the foam of the invention.)

[0029] The preferred blowing agent used is isobutane. One or more conventional or useful blowing agents can be used. Such other suitable volatile blowing agents include halocarbons such as fluorocarbons and chlorofluorocarbons; hydrohalocarbons such as hydrofluorocarbons and hydrochlorofluorocarbons, such as, dichlorotetrafluoroethane, dichlorodifluoroethane, dichloromonofluoromethane and trichloromonofluoromethane; alkylhalides, such as methyl chloride and ethyl chloride; hydrocarbons such as alkanes or alkenes; carbon dioxide, nitrogen, argon, and water. Examples of useful alkanes having from 2 to 9 carbon atoms are ethane, propane, butane, pentane, isopentane, hexane, isohexane, and heptane.

[0030] The invention foam structure is formed by the extrusion accumulator process disclosed in U.S. Patent No. 4,323,528. The process for producing large size, low or high density, elongated thermoplastic cellular bodies includes the forming of a mixture of a thermoplastic polymer-copolymer blend composition and the isobutane blowing agent dissolved therein under pressure and at a temperature at which the viscosity of the mixture is sufficient to retain the isobutane blowing agent when the mixture is allowed to expand. The mixture is extruded into a holding zone under conditions that prevent the mixture from foaming. The holding zone has an outlet die orifice opening into a zone of lower pressure and temperature at which the mixture foams. The outlet die orifice must be designed to allow the expansion of the fine celled foam to the appropriate stated width dimensions. An openable gate closes the die orifice. Periodically the gate is opened and substantially concurrently mechanical pressure is applied by a movable ram on the mixture, preferably while scraping the sides of the holding zone with the ram, to eject the mixture from the holding zone through the die orifice at a rate in excess of that at which substantial foaming in the die orifice occurs and less than that at which substantial irregularities in the cross-sectional area or shape of the cellular body occurs, preferably 4,082 kg/hour (9,000 lb/hour) to 4,990 kg/hour (11,000 lb/hour), most preferably the foam ejection rate of 4,763 kg/hour (10,500 lb/hour). The ejected mixture is permitted to expand unrestrained in at least one dimension to produce the elongated thermoplastic cellular body. The apparatus for producing elongated thermoplastic cellular bodies includes an extruder for feeding a mixture of the thermoplastic polymer blend and the plasticizing isobutane blowing agent at

a temperature suitable for producing a cellular body when the mixture is subjected to lower pressure, and an expandable holding chamber receiving the mixture from the extruder and maintaining the mixture in a molten state at a pressure above the foaming pressure thereof. There is a ram means for ejecting the mixture out of the holding chamber, a die having an orifice, preferably in line with the ram means, through which the mixture is ejected from the holding chamber by operation of the ram means, and gate means contacting the exterior surface of the die for closing and sealing the die orifice while the holding chamber is being filled.

[0031] The conditions in the extruder portion of the extrusion-accumulator apparatus for the invention foam typically are:

Temperatures: Feed/Metering: 149° to 219° (300° to 425°), preferably 160° to 205°C (320° to 400°F)
Colling: 49° to 110°C (120° to 230°F), preferably 66° to 82°C (150° to 180°F)
Pressures: 4.14 to 13.79 MPa (600 to 2000 psi), preferably 4.48 to 6.89 MPa (650 to 1,000 psi).

[0032] The conditions in the accumulator for the invention foam typically are:

Temperatures: 88° to 107°C (190° to 225°F), preferably 99° to 105°C (210° to 221°F).
Pressures: 1.38 to 6.89 MPa (200 to 1,000 psi), preferably 2.76 to 4.14 MPa (400 to 600 psi).

[0033] Extruded foam planks with cell size typically of the herein stated invention formed by extrusion using an extruder with an extrusion die, in the case of uncrosslinked PE or PE/EVA, have surface ripples, corrugations, warping and the like. To the contrary, the non-crosslinked PE/EVA or PE/EMA foam planks of the invention, which are formed by the extrusion accumulator system, do not have surface ripples, corrugations or warping. The foam planks of the invention have smooth flat surfaces. The invention process produces microcellular or fine celled foam structures and planks with cell counts usually within the range of 19.7 to 47.2 cells/cm (50 to 120 cpi), ideally greater than 27.6 cells/cm than (70 cpi). The invention foam planks are substantially composed of closed cells.

[0034] The process and polymer blend compositions of the invention are particularly useful in producing polyolefin foam planks, especially polyethylene foam planks. For example, low density polyethylene foam with a density in the range of 19.2 to 41.7 kg/m³ (1.2 to 2.6 pcf) can be produced. The foam has a fine-celled closed structure containing greater than 19.7 cells/cm (50 cells per inch). The foam is made in plank form with finished nominal dimensions of 5.7 cm by 61.0 cm by 274 cm (2 1/4 inches by 24 inches by 108 inches). Using the accumulator process, as described in U.S. Patent No. 4,323,528, such flat foamed plank structure has been produced. Another example is that low density polyethylene foam planks having the same specifications as the preceding foam planks except that the finished nominal dimensions are 8.3 cm by 61 cm by 274 cm (3 1/4 inches by 24 inches by 108 inches). Foam planks can be made in varying widths and length. High density polyethylene foam planks having a density of 64.1 kg/m³ (4 pcf) or greater can be produced by the invention process and from the invention polymer blend compositions.

[0035] To accelerate the release of the isobutane blowing agent from the ejected thermoplastic foam, the ejected thermoplastic foam can be subjected to heat below any level having adverse effect on the thermoplastic foam or can be perforated so as to create a series of narrow channels in and/or through the thermoplastic foam.

[0036] The invention thermoplastic foams are recyclable in that the basic chemical nature of thermoplastic usually does not change significantly as a result of the extrusion process. Thermoplastic materials can generally be reground and recycled into a usable form. Thermosets undergo a crosslinking reaction when the temperature is raised above a certain point. The crosslinking forms a three dimensional network which remains intact when the temperature is reduced. This causes an irreversible change in the material and, therefore, can not be recycled like thermoplastic materials.

[0037] By way of summary, the product is a polyolefin foam with a density in the range of 19.2 to 144.2 kg/m³ (1.2 and 9.0 pcf). The polyolefin foam planks can be low density, e.g., density of 19.2 to 41.7 kg/m³ (1.2 to 2.6 pcf), or high density, e.g., density of 64.1 to 144.2 kg/m³ (4.0 to 9.0 pcf). The polyolefin is usually low density polyethylene. The foam is made in plank form, e.g., with nominal dimensions of 61 cm x 274 cm x 5.1 to 8.9 cm (24 inches x 108 inches x 2 to 3 1/2 inches). The foam has a fine-celled structure containing 19.7 to 47.2 cells/cm (50 to 120 cells per inch (cpi)). Using the accumulator process as described in U.S. Patent No. 4,323,528, the invention process is able to produce a flat foamed plank structure. The foam is a non-crosslinked thermoplastic material and is recyclable, unlike crosslinked foam. Like crosslinked foam, the invention foam is smooth to the touch and passes the surface abrasion resistance as required of the packaging of Class A surfaces. This invention foam is physically comparable with a crosslinked foam product with recyclability as an added bonus. The invention foam can be white or colored and can also contain additives, such as, UV stabilizers, antistats, pigments, and antioxidants. To improve softness, ethylene copolymers containing esters such as ethylene vinyl acetate (EVA) or ethylene methyl acrylate (EMA) can be added to the LDPE. The total ester monomer content of the final product (excluding the blowing agent) is in the range of 0.1 to 10 (or 20) percent. To improve stiffness of the ester modified foam, an ionomeric resin can be added in the range of

up to 5 percent [e.g., 0.01 to 5 (or 10) percent]. The invention foam is preferably made with a crystalline silica nucleating agent or a sodium bicarbonate nucleating agent or a talc nucleating agent, and isobutane as the sole blowing agent. Glycerol monostearate (most preferred) or a similar fatty acid compound can be used as the permeability control agent.

[0038] A comparison of prior art crosslinked foam materials with invention non- crosslinked foam materials follows:

MATERIALS					
PROPERTIES	Sentinel MC1900e xipe/eva literature	Sentinel MC1900 xipe literature	Inven. PE/EMA 2 wk test	Inven. PE/EVA 2 wk test	Inven. PE/EVA/lonomer 4 wk test
Density kg/m ³ (pcf)	32.0 (2)	32.0 (2)	32.0 (2)	32.0 (2)	32.0 (2)
cells/cm (CPI)	66.5 (169)	66.5 (169)	27.6-31.5 (70-80)	27.6-31.5 (70-80)	27.6-31.5 (70-80)
Comp. Strength 25%	4.5	8.5	7.6	6	8.2
Comp. Sets	20	15	12.5	19	15.6
Tensile Strength KPa (psi)	345 (50)	276 (40)		303 (44)	
Tear Resistance (pli)	8	7		10	
Water Absorption (ps)	0.05 max	0.05 max		<0.05	
Therm. Stab. % shrink CMD			<3%	<2%	<2.5%
MD	<2%	<2%	<3%	<2%	<3.5%
Thickness			<3%	<3%	<5%
Die Cut, % CMD	<2%		<2%	<2%	<2%
MD	<2%		<2%	<2%	<2%
Thickness	<4%		<2%	<4%	<2.5%

Claims

1. A process for preparing a non-crosslinked polyolefin foam elongated cellular body having a fine-celled closed structure, said fine-celled structure having a cell count greater than 19.7 cells/cm (50 cells/inch), said process comprising the steps of melting a polyolefin; forming a mixture of said polyolefin, and an amount of a fatty acid compound permeability control agent; dissolving an effective amount of a blowing agent in said mixture to form a blowing agent-containing mixture; transferring said blowing agent-containing mixture into a zone of lower pressure and temperature; and permitting said blowing agent-containing mixture to expand in the zone of lower pressure and temperature to produce said elongated cellular body, said process being **characterized by** the steps of:

melting a copolymer of an olefin monomer and an ethylenic monomer different from the monomer of said polyolefin with said polyolefin to form a polymeric blend before the step of forming said mixture, the amount of said copolymer being in the range of from 5 to 25 percent by weight of said blend;

adding an amount of a nucleating agent sufficient to produce a cell count greater than 19.7 cells/cm (50 cells/inch) to said mixture before the step of dissolving said blowing agent; and

after said step of dissolving, extruding said blowing agent-containing mixture into a holding zone; and maintaining said holding zone at conditions, including temperature and pressure, at which said blowing agent-

containing mixture does not foam.

2. The process of claim 1 wherein said polyolefin is selected from the group consisting of polyethylene and polypropylene.
3. The process of claim 2 wherein said polyethylene is selected from the group consisting of HDPE, MDPE, LDPE and LLDPE.
4. The process of claim 1 wherein said copolymer is selected from the group consisting of ethylene vinyl acetate and ethylene methyl acrylate.
5. The process of claim 1 wherein said fatty acid is selected from the group consisting of amides and esters of C₁₂₋₂₄ fatty acids.
6. The process of claim 5 wherein said fatty acid is selected from the group consisting of steryl stearamide, glycerol monostearate, glycerol monobehenate, and sorbitol monostearate.
7. The process of claim 6 wherein said fatty acid is glycerol monostearate.
8. The process of claim 1 wherein said nucleating agent is selected from the group consisting of crystalline silica, sodium bicarbonate and citric acid, talc, clay, mica, titanium oxide, zinc oxide, calcium silicate, barium stearate, zinc stearate and aluminum stearate.
9. The process of claim 8 wherein said nucleating agent is selected from the group consisting of crystalline silica, sodium bicarbonate and talc.
10. The process of claim 9 wherein said nucleating agent is crystalline silica.
11. The process of claim 1 wherein said cell count is from 19.7 to 47.2 cells/cm (50 to 120 cells/inch).
12. The process of claim 1 wherein said cell count is greater than 27.6 cells/cm (70 cells/inch).
13. The process of claim 1 wherein said ethylenic monomer being in the amount of from 5 to 20 percent by weight of said copolymer.
14. The process of claim 1 wherein the step of expanding in the zone of lower pressure and temperature further includes expanding unrestrained in at least one dimension.
15. The process of claim 1 wherein said elongated cellular body is a foam plank.
16. The process of claim 15 wherein said foam plank has a density of from 19.2 to 41.6 kg/m³ (1.2 to 2.6 pounds per cubic foot).
17. The process of claim 15 wherein said foam plank has a density of from 64.1 to 144.2 kg/m³ (4.0 to 9.0 pounds per cubic foot).
18. The process of claim 1 wherein said blowing agent is selected from the group consisting of halocarbons, hydrohalocarbons, alkylhalides, hydrocarbons, carbon dioxide, nitrogen, argon, and water.
19. The process of claim 18 wherein said blowing agent is a hydrocarbon, said hydrocarbon being selected from the group of alkanes and alkenes, said group of alkanes being selected from the group consisting of ethane, propane, butane, isobutane, pentane, isopentane, hexane, isohexane, and heptane.
20. The process of claim 19 wherein said blowing agent is isobutane.
21. The process of claim 1 wherein said mixture further includes an ionomer to improve the strength of said elongated cellular body.

22. The process of claim 1 wherein said polyolefin is low density polyethylene, said copolymer is selected from the group consisting of ethylene vinyl acetate and ethylene-methyl acrylate, said fatty acid is glycerol monostearate and said nucleating agent is selected from the group consisting of crystalline silica, sodium bicarbonate and citric acid, and talc.

23. A non-crosslinked fine-celled foam product comprising:

a polymeric structure being substantially composed of fine cells and having the cell count being greater than 19.7 cells/cm (50 cells/inch), said polymeric structure being a blend of a polyolefin and a copolymer of an olefin monomer and an ethylenic monomer different from the monomer of said polyolefin, the amount of said copolymer being in the range of from 5 to 25 percent by weight of said blend.

24. The product of claim 23 wherein said product is an elongated cellular body.

25. The product of claim 23 wherein said product is a foam plank.

26. The product of claim 25 wherein said foam plank has a density of from 19.2 to 41.6 kg/m³ (1.2 to 2.6 pounds per cubic foot).

27. The product of claim 25 wherein said foam plank has a density of from 64.1 to 144.2 kg/m³ (4.0 to 9.0 pounds per cubic foot).

28. The product of claim 23 wherein the cell count is from 19.7 to 47.2 cells/cm (50 to 120 cells/inch).

29. The product of claim 23 wherein the cell count is greater than 27.6 cells/cm (70 cells/inch).

30. The product of claim 23 wherein said foam product is recyclable.

Patentansprüche

1. Verfahren zum Herstellen eines länglichen, zellenartigen Körpers aus nichtvernetztem Polyolefin-Schaum, der eine feinzellige geschlossene Struktur aufweist, wobei die feinzellige Struktur eine Zellenanzahl größer als 19,7 Zellen/cm (50 Zellen/inch) aufweist, wobei das Verfahren die Schritte umfasst, dass man ein Polyolefin schmilzt; eine Mischung aus dem Polyolefin und einer Menge einer Fettsäure-Verbindung als einem die Permeabilität steuernden Mittel mischt; eine wirksame Menge eines Treibmittels in der Mischung löst, um eine Treibmittel enthaltende Mischung zu bilden; die Treibmittel enthaltende Mischung in eine Zone niedrigeren Drucks und niedrigerer Temperatur überführt; und die Treibmittel enthaltende Mischung in der Zone niedrigeren Drucks und niedrigerer Temperatur expandieren lässt, um den länglichen zellenartigen Körper herzustellen, worin das Verfahren durch die Schritte gekennzeichnet ist, dass man:

- ein Copolymer aus einem Olefin-Monomer und einem ethylenischen Monomer, das verschieden ist von dem Monomer des Polyolefins, mit dem Polyolefin schmilzt, um eine Polymermischung vor dem Schritt des Bildens der Mischung zu bilden, wobei die Menge des Copolymers im Bereich von 5 bis 25 Gew.-% der Mischung liegt;
- eine Menge eines Nukleierungsmittels, die ausreichend ist, um eine Zellenanzahl größer als 19,7 Zellen/cm (50 Zellen /inch) zu erzeugen, dieser Mischung vor dem Schritt des Lösens des Treibmittels zusetzt; und
- nach dem Schritt des Lösens die Treibmittel enthaltende Mischung in einer Haltezone extrudiert; und
- die Haltezone unter Bedingungen, einschließlich Temperatur und Druck, hält, bei denen die Treibmittel enthaltende Mischung nicht schäumt.

2. Verfahren nach Anspruch 1, worin das Polyolefin ausgewählt ist aus der Gruppe, die besteht aus Polyethylen und Polypropylen.

3. Verfahren nach Anspruch 2, worin das Polyethylen ausgewählt ist aus der Gruppe, die besteht aus HDPE, MDPE, LDPE und LLDPE.

4. Verfahren nach Anspruch 1, worin das Copolymer ausgewählt ist aus der Gruppe, die besteht aus Ethylenvinylacetat und Ethylenmethacrylat.

5. Verfahren nach Anspruch 1, worin die Fettsäure ausgewählt ist aus der Gruppe, die besteht aus Amiden und Estern von C₁₂₋₂₄-Fettsäuren.
- 5 6. Verfahren nach Anspruch 5, worin die Fettsäure ausgewählt ist aus der Gruppe, die besteht aus Stearylstearamid, Glycerinmonostearat, Glycerinmonobehenat und Sorbitolmonostearat.
7. Verfahren nach Anspruch 6, worin die Fettsäure Glycerinmonostearat ist.
- 10 8. Verfahren nach Anspruch 1, worin das Nukleierungsmittel ausgewählt ist aus der Gruppe, die besteht aus kristallinem Siliciumoxid, Natriumbicarbonat und Citronensäure, Talk, Ton, Glimmer, Titanoxid, Zinkoxid, Calciumsilicat, Bariumstearat, Zinkstearat und Aluminiumstearat.
- 15 9. Verfahren nach Anspruch 8, worin das Nukleierungsmittel ausgewählt ist aus der Gruppe, die besteht aus kristallinem Siliciumoxid, Natriumbicarbonat und Talk.
10. Verfahren nach Anspruch 9, worin das Nukleierungsmittel kristallines Siliciumoxid ist.
- 20 11. Verfahren nach Anspruch 1, worin die Zellenanzahl im Bereich von 19,7 bis 47,2 Zellen/cm (50 bis 120 Zellen/inch) liegt.
12. Verfahren nach Anspruch 1, worin die Zellenanzahl größer ist als 27,6 Zellen/cm (70 Zellen/inch).
- 25 13. Verfahren nach Anspruch 1, worin das ethylenische Monomer in einer Menge von 5 bis 20 Gew.-% des Copolymers zugegen ist.
14. Verfahren nach Anspruch 1, worin der Schritt der Expansion in der Zone niedrigeren Drucks und niedrigerer Temperatur darüber hinaus die ungehinderte Expansion in wenigstens eine Dimension einschließt.
- 30 15. Verfahren nach Anspruch 1, worin der längliche zellenartige Körper ein Brett aus Schaum ist.
16. Verfahren nach Anspruch 15, worin das Brett aus Schaum eine Dichte von 19,2 bis 41,6 kg/m³ (1,2 bis 2,6 pounds per cubic foot) aufweist.
- 35 17. Verfahren nach Anspruch 15, worin das Brett aus Schaum eine Dichte von 64,1 bis 144,2 kg/m³ (4,0 bis 9,0 pounds per cubic foot) aufweist.
- 40 18. Verfahren nach Anspruch 1, worin das Treibmittel ausgewählt ist aus der Gruppe, die besteht aus Halogenkohlenstoffen, Halogenkohlenwasserstoffen, Alkylhalogeniden, Kohlenwasserstoffen, Kohlendioxid, Stickstoff, Argon und Wasser.
19. Verfahren nach Anspruch 18, worin das Treibmittel ein Kohlenwasserstoff ist, wobei der Kohlenwasserstoff ausgewählt ist aus der Gruppe, die besteht aus Alkanen und Alkenen, die Gruppe von Alkanen ausgewählt ist aus der Gruppe, die besteht aus Ethan, Propan, Butan, Isobutan, Pentan, Isopentan, Hexan, Isohexan und Heptan.
- 45 20. Verfahren nach Anspruch 19, worin das Treibmittel Isobutan ist.
21. Verfahren nach Anspruch 1, worin die Mischung darüber hinaus ein Ionomer einschließt, um die Festigkeit des länglichen, zellenartigen Körpers zu verbessern.
- 50 22. Verfahren nach Anspruch 1, worin das Polyolefin Polyethylen niedriger Dichte ist, das Copolymer ausgewählt ist aus der Gruppe, die besteht aus Ethylenvinylacetat und Ethylenmethacrylat, die Fettsäure Glycerinmonostearat ist und das Nukleierungsmittel ausgewählt ist aus der Gruppe, die besteht aus kristallinem Siliciumoxid, Natriumbicarbonat und Citronensäure und Talk.
- 55 23. Ein nicht-vernetztes, feinzelliges Schaumprodukt, umfassend:
 - eine Polymerstruktur, die im wesentlichen aus feinen Zellen zusammengesetzt ist und die eine Zellenanzahl aufweist, die größer als 19,7 Zellen/cm (50 Zellen/inch) ist, wobei die Polymerstruktur eine Mischung aus

einem Polyolefin und einem Copolymer aus einem Olefin-Monomer und einem ethylenischen Monomer ist, das verschieden ist von dem Monomer des Polyolefins, und die Menge des Copolymers im Bereich von 5 bis 25 Gew.-% der Mischung liegt.

- 5 24. Produkt nach Anspruch 23, worin das Produkt ein länglicher, zellenartiger Körper ist.
25. Produkt nach Anspruch 23, worin das Produkt ein Brett aus Schaum ist.
- 10 26. Produkt nach Anspruch 25, worin das Brett aus Schaum eine Dichte von 19,2 bis 41,6 kg/m³ (1,2 bis 2,6 pounds per cubic foot) aufweist.
27. Produkt nach Anspruch 25, worin das Brett aus Schaum eine Dichte von 64,1 bis 144,2 kg/m³ (4,0 bis 9,0 pounds per cubic foot) aufweist.
- 15 28. Produkt nach Anspruch 23, worin die Zellenanzahl im Bereich von 19,7 bis 47,2 Zellen/cm (50 bis 120 Zellen/inch) liegt.
29. Produkt nach Anspruch 23, worin die Zellenanzahl größer ist als 27,6 Zellen/cm (70 Zellen/inch).
- 20 30. Produkt nach Anspruch 23, worin das Schaumprodukt wieder verwertbar ist.

Revendications

- 25 1. Procédé pour préparer un corps cellulaire allongé en mousse de polyoléfine non réticulée possédant une structure fermée à cellules fines, ladite structure à cellules fines possédant une numération cellulaire supérieure à 19,7 cellules/cm (50 cellules/pouce), ledit procédé comprenant les étapes de fusion d'une polyoléfine ; de formation d'un mélange de ladite polyoléfine, et d'une quantité d'un agent de contrôle de la perméabilité qui est un composé d'acide gras ; de dissolution d'une quantité efficace d'un agent gonflant dans ledit mélange afin de former un
30 mélange contenant un agent gonflant ; de transfert dudit mélange contenant un agent gonflant dans une zone de pression et de température inférieure ; et gonflant dudit mélange contenant un agent gonflant dans la zone de pression et de température inférieure afin de produire ledit corps cellulaire allongé, ledit procédé étant **caractérisé par** les étapes de :
35 fusion d'un copolymère d'un monomère d'oléfine et d'un monomère éthylénique différent du monomère de ladite polyoléfine avec ladite polyoléfine afin de former un mélange polymère avant l'étape de formation dudit mélange, la quantité dudit copolymère étant de l'ordre de 5 à 25 pour cents par poids dudit mélange ;
addition d'une quantité d'un agent de nucléation suffisante pour produire une numération cellulaire supérieure à 19,7 cellules/cm (50 cellules/pouce) audit mélange avant l'étape de dissolution dudit agent gonflant ; et
40 après ladite étape de dissolution, extrusion dudit mélange contenant un agent gonflant dans une zone de rétention ; et
maintien de ladite zone de rétention dans des conditions, comprenant la température et la pression, auxquelles ledit mélange contenant un agent gonflant ne mousse pas.
- 45 2. Procédé selon la revendication 1, dans lequel ladite polyoléfine est choisie dans le groupe constitué du polyéthylène et du polypropylène.
3. Procédé selon la revendication 2, dans lequel ledit polyéthylène est choisi dans le groupe constitué par le HDPE, le MDPE, le LDPE et le LLDPE.
- 50 4. Procédé selon la revendication 1, dans lequel ledit copolymère est choisi parmi le groupe constitué par l'éthylène-acétate de vinyle et l'éthylène-acrylate de méthyle.
5. Procédé selon la revendication 1, dans lequel ledit acide gras est choisi parmi le groupe constitué par les amides et les esters des acides gras en C₁₂₋₂₄.
- 55 6. Procédé selon la revendication 5, dans lequel ledit acide gras est choisi dans le groupe constitué par le stéaryl stéaramide, le monostéarate de glycérol, le monobéhénate de glycérol, et le monostéarate de sorbitol.

7. Procédé selon la revendication 6, dans lequel ledit acide gras est le monostéarate de glycérol.
8. Procédé selon la revendication 1, dans lequel ledit agent de nucléation est choisi dans le groupe constitué par la silice cristalline, le bicarbonate de sodium et l'acide Citrique, le talc, l'argile, le mica, l'oxyde de titane, l'oxyde de zinc, le silicate de calcium, le stéarate de baryum, le stéarate de zinc et le stéarate d'aluminium.
9. Procédé selon la revendication 8, dans lequel ledit agent de nucléation est choisi dans le groupe constitué par la silice cristalline, le bicarbonate de sodium et le talc.
10. Procédé selon la revendication 9, dans lequel ledit agent de nucléation est la silice cristalline.
11. Procédé selon la revendication 1, dans lequel ladite numération cellulaire est de 19,7 à 47,2 cellules/cm (50 à 120 cellules/pouce).
12. Procédé selon la revendication 1, dans lequel ladite numération cellulaire est supérieure à 27,6 cellules/cm (70 cellules/pouce).
13. Procédé selon la revendication 1, dans lequel ledit monomère éthylénique est dans une quantité de 5 à 20 pour cents en poids dudit copolymère.
14. Procédé selon la revendication 1, dans lequel l'étape gonflant dans la zone de pression et de température inférieure comprend en outre une expansion non restreinte dans au moins une dimension.
15. Procédé selon la revendication 1, dans lequel ledit corps cellulaire allongé est un plateau en mousse.
16. Procédé selon la revendication 15, dans lequel ledit plateau en mousse a une masse volumique de 19,2 à 41,6 kg/m³ (1,2 à 2,6 livres par pied cube).
17. Procédé selon la revendication 15, dans lequel ledit plateau en mousse possède une masse volumique de 64,1 à 144,2 kg/m³ (4,0 à 9,0 livres par pied cube).
18. Procédé selon la revendication 1, dans lequel ledit agent gonflant est choisi dans le groupe constitué par les hydrocarbures halogénés, les hydrocarbures partiellement halogénés, les halogénures d'alkyle, les hydrocarbures, le dioxyde de carbone, l'azote, l'argon et l'eau.
19. Procédé selon la revendication 18, dans lequel ledit agent gonflant est un hydrocarbure, ledit hydrocarbure étant choisi dans le groupe constitué par les alcanes et les alcènes, ledit groupe des alcanes étant choisi dans le groupe constitué par l'éthane, le propane, le butane, l'isobutane, le pentane, l'isopentane, l'hexane, l'isohexane, et l'heptane.
20. Procédé selon la revendication 19, dans lequel ledit agent gonflant est l'isobutane.
21. Procédé selon la revendication 1, dans lequel ledit mélange contient en outre un ionomère pour améliorer la résistance dudit corps cellulaire allongé.
22. Procédé selon la revendication 1, dans lequel ladite polyoléfine est un polyéthylène à basse densité, ledit copolymère est choisi dans le groupe constitué par l'éthylène-acétate de vinyle et l'éthylène-acrylate de méthyle, ledit acide gras est le monostéarate de glycérol et ledit agent de nucléation est choisi dans le groupe constitué par la silice cristalline, le bicarbonate de sodium et l'acide citrique, et le talc.
23. Produit en mousse à cellules fines non réticulée comprenant :

une structure polymère étant sensiblement composée de cellules fines et possédant la numération cellulaire supérieure à 19,7 cellules/cm (50 cellules/pouce), ladite structure polymérique étant un mélange d'une polyoléfine et d'un copolymère d'un monomère d'oléfine et d'un monomère éthylénique différent du monomère de ladite polyoléfine, la quantité dudit copolymère étant dans la gamme de 5 à 25 pour cents en poids dudit mélange.

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24. Produit selon la revendication 23, dans lequel ledit produit est un corps cellulaire allongé.

25. Produit selon la revendication 23, dans lequel ledit produit est un plateau en mousse.

5 **26.** Produit selon la revendication 25, dans lequel ledit plateau en mousse a une masse volumique de 19,2 à 41,6 kg/m³ (1,2 à 2,6 livres par pied cube).

27. Produit selon la revendication 25, dans lequel ledit plateau en mousse a une masse volumique de 64,1 à 144,2 kg/m³ (4,0 à 9,0 livres par pied cube).

10 **28.** Produit selon la revendication 23, dans lequel la numération cellulaire est de 19,7 à 47,2 cellules/cm (50 à 120 cellules/pouce).

29. Produit selon la revendication 23, dans lequel la numération cellulaire est supérieure à 27,6 cellules/cm (70 cellules/pouce).

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30. Produit selon la revendication 23, dans lequel ledit produit en mousse est recyclable.

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